USNRDL-TR-67-128
10 September 1967

CONCENTRATION OF MIXED FISSION PRODUCTS FROM SEAWATER BY CHELEX 100

by

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The work reported is a part of a project sponsored by the Advanced Research Projects Agency under Order No. 961, Amendment 1, Program Code 7F40.

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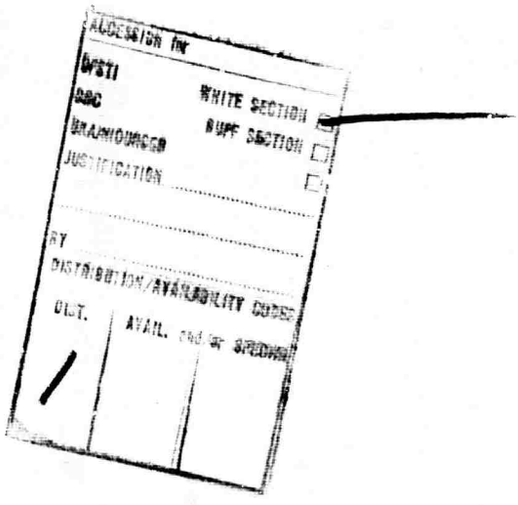

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ABSTRACT

A study was conducted to determine the feasibility of concentrating mixed fission products in seawater by ion-exchange. Chelex 100, a chelating resin, was found to be effective for the concentration of several gamma-emitting fission-product radionuclides from seawater.

The effects of fission-product age, total seawater volume, and flow rate on adsorption were studied.

SUMMARY

Problem

The purpose of this investigation was to determine the effectiveness of Chelex 100, a chelating ion-exchange resin, for concentrating mixed fission products from seawater. This is the first step in the development of extremely sensitive continuous *in situ* radiochemical separation and counting techniques to be used in location and identification of surface and subsurface radioactive materials.

Findings

1. Nd^{147}, $Ce^{141,143,144}$ and La^{140} were the only gamma-emitting fission products found to be strongly adsorbed by Chelex 100. However, these were among the most abundant contributors to the gamma spectrum of fission products in the time period 5 to 160 days after fission.

2. The total fraction of the radionuclide gamma activity retained by the Chelex 100 column varied from 34 % at relatively early times after fission (5 days) to a maximum of 50 % at 30-40 days and then decreased to 36 % at 157 days after fission.

3. There was essentially no change in the adsorption efficiency of the Chelex 100 column for seawater volumes up to and including 20 liters, the largest sample size that was run in these tests (with 52-day-old fission product mixture) at a flow rate of 8 ml/cm^2-min.

4. Adsorption of La^{140}, a major component of the fission product gamma spectrum from 5 to 80 days after fission, was nearly quantitative

at flow rates below 12 ml/cm^2-min. For higher flow rates, leakage generally increased linearly with the volume of sample passed through the column. The percent leakage increased with an increase in the flow rate.

5. The basis for the desired in situ concentration system thus exists.

INTRODUCTION

A program has been established at this Laboratory for the development of an *in situ* analysis system for the identification of fission product radioactivity in the ocean. Such a system is required for the monitoring of ocean areas for radioactive materials.

Several workers have considered this problem of finding low levels of fission product activities in seawater.[1,2,3,4] The method used in these studies involved the location of radioactive waters by means of an *in situ* crystal probe coupled to a gross gamma counter or to a gamma pulse-height spectrometer. Within its sensitivity range (which is limited by, among other factors, the natural background activity contributed by K^{40}) the method offers a promising approach. However, if one needs to locate smaller amounts of radioactivity, identify and quantitate specific nuclides, or reduce "on-station" counting times, some type of concentration of the radioactivity is necessary.

BACKGROUND

Seawater concentration methods presently being used include: (1) removal of water from the sample, by evaporation or freeze drying of the water from the sample,[5] (2) co-crystallization (a process that

involves direct crystallization) from an aqueous solution of an organic reagent which combines with the trace element of interest, without the addition of carrier,[6,7] (3) coprecipitation, the removal of the trace element of interest by use of a scavenger such as ferric hydroxide,[8] bismuth phosphate,[9] etc., (4) solvent extraction, a process in which the trace element is concentrated by extraction into a second, immiscible liquid phase,[10] and (5) sorption, including ion-exchange, a process in which the trace element is extracted by sorption onto a solid phase.[11,12]

Of the above concentration methods the sorption method appears to be the most adaptable to a fast-reacting, in situ system. Concentration by ion-exchange, provided the proper resin can be found, would involve minimum manipulation since the water sample would simply be pumped through the resin column to extract the radionuclide activity. The resin column could be coupled to a gamma-counting or spectrometer system that would assay the extracted activity.

One material presently under study at this Laboratory is Chelex 100 (a processed form of Dowex Resin A-1), a chelating ion-exchange resin that has been found to have an unusually high preference for copper, cobalt and other heavy metals over such cations as sodium, potassium, magnesium, and calcium.[13] In studies conducted at NRDL[11,12], cobalt and plutonium have been successfully extracted from seawater by use of this resin. It was expected that other trace elements, including a number of fission product radionuclides, could be successfully concentrated with the resin. Preliminary studies, utilizing a limited bath technique, have indicated that the following elements are strongly adsorbed by the resin: Ni, Zn, Ce, La, Tm, Pb, Am, Tb, Mn, Bi, Pu, Cr, Th, Co, Cd, Fe, and Hg.[14] The present study utilizes an ion-exchange column to effect the concentration of the desired radionuclides from relatively large volumes of seawater.

APPROACH

Seawater samples containing radionuclide gamma activity (primarily mixed fission products) were processed through a column of Chelex 100 resin. The adsorbed radionuclide gamma activity was then eluted from the column and identified. Several parameters were studied. These included the effect of the age of the fission product mixture, the effect of seawater volume and the effect of flow rate on column efficiency.

EXPERIMENTAL

Materials

1. Resin: 50-100 mesh Chelex 100, a chelating ion exchange resin, produced by Bio-Rad Laboratories, Richmond, California.

2. Seawater: Natural Pacific Coast seawater, salinity $35^{o}/_{oo}$, filtered through a 0.45-μ membrane filter (Millipore) just prior to use.

3. Fission products: Obtained by thermal neutron activation of uranium nitrate. A stock solution was made by dissolving the solid uranium nitrate and fission products in a liter of seawater. The solution was stored in a teflon container.

4. La^{140} radioactive tracer obtained from Nuclear Science and Engineering Corp.

Apparatus

1. Ion-Exchange Column: The ion exchange column consisted of a Pyrex tube (11.5 cm long and 1.8 cm i.d.) closed at the bottom by a teflon stopcock. The upper end of the tube was connected to a sample reservoir by a length of tygon tubing. The column was filled to an initial height of 10 cm with a water slurry of approximately 25 gm

(wet weight) of distilled water-washed Chelex 100 resin. The column was further washed by passing through of 0.5 liters of natural seawater. The washing caused the resin column to shrink to about half its original length (to ~ 5 cm) and lowered the resin pH to approximately 8. A glass wool plug was placed on top of the Chelex 100 to prevent erosion of the resin bed during sample addition.

2. Well scintillation counter system: 3 x 3-in. NaI(Tl) crystal mounted on an NRDL-designed preamplifier encased in a lead shield of 2-in. overall thickness.

3. Pulse Height Analyzer System: 3 x 3-in. cylindrical NaI(Tl) crystal mounted on a modified Technical Measurements Corporation (TMC) preamplifier and encased in a lead shield of 2-in. overall thickness. The analyzer was a TMC 400-channel analyzer, Model 404-6.

Procedure

Samples were prepared just prior to each experimental run by addition of radionuclide activity from the stock solution to filtered natural seawater contained in a polyethylene carboy. The solution was stirred vigorously for 1/2 hr before passage through the resin column. Flow rates were controlled at 8 ml/cm^2-min except for the flow rate study, in which higher flow rates were used.

1. Identification of Gamma-Emitting Radionuclides in Fission Product Mixtures Before and After Adsorption by Chelex 100.

Five-liter seawater samples were passed through the column at 5, 22, 52 and 157 days after fission. The radionuclide gamma activities adsorbed by the column were eluted with 100 ml of 4N HCl. Aliquots of this eluate were analyzed by pulse-height gamma spectrometry; the results were then compared with those from aliquots of the original, unprocessed samples.

2. Adsorption of Mixed Fission Products from Seawater at Designated Times After Fission.

Five-liter seawater samples were prepared from fission product mixtures aged to 5, 22, 39, 50, 66, 77, 91, 123 and 157 days after fission. After passage of the solution through the resin column, the adsorbed radionuclide activities were eluted with 4N HCl. For each time, the percent gamma activity adsorbed by the resin was determined by comparison with the count from an aliquot of the unprocessed solution.

3. Adsorption of Fission Products From Different Volumes of Seawater.

Samples were prepared from a fission product mixture aged to 52 days after fission. Seawater samples of 1, 5 and 20 liters were passed through a Chelex 100 column. After passage of each sample through the column, the adsorbed activity was eluted with 4N HCl and an aliquot was counted. The percent gamma activity adsorbed was calculated for each sample volume.

4. Effect of Flow Rate on the Efficiency of the Chelex 100 Column; La^{140} as Simulant for Fission Product Activity.

La^{140} was used as a substitute for mixed fission products in these studies. This was done to simplify the interpretation of the results of flow rate experiments. La^{140} had been shown previously to be one of the three gamma-emitting isotopes of mixed fission products that were strongly adsorbed (> 99 %) by Chelex 100.[14]

Seawater samples of 10 to 20 liters containing La^{140} tracer were passed through a Chelex 100 column at flow rates of 12, 26, 60 and 120 ml/cm^2-min. Aliquots of the effluent were analyzed at 1 liter intervals. The percent leakage was determined from a comparison of the count with that from an aliquot of the solution that had not been processed through the column.

RESULTS AND DISCUSSION

1. Identification of Gamma-Emitting Radionuclides in Fission Product Mixtures Before and After Adsorption by Chelex 100.

The results are shown in Figs. 1-4.

The upper curve of each figure shows the gamma spectrum of fission-product-spiked seawater samples before passage through the Chelex 100 column; the lower curve, an aliquot of the 4N-HCl eluate obtained after passage of the 5-liter samples.

At the early time (5 days) the gamma spectrum of the spiked seawater was relatively complex, with identifiable peaks of Nd^{147} ($t_{1/2}$ 11.1 da), Ce^{141} (32.5 da), Mo^{99} (66 hr), Te^{132} (78 hr), Ce^{143} (33 hr), La^{140} (40.2 hr from 12.8 da parent), I^{133} (21 hr), and I^{132} (2.3 hr from 78 hr parent).

At 22 days several of the shorter-lived components (i.e. Mo^{99}, Te^{132}, Ce^{143}, I^{132}, and I^{133}) had decayed. However, several other nuclides (Zr^{95} (65 da) - Nb^{95} (35 da), and Ru^{103} (40 da)) were detected.

At 52 days only Nd^{147}, Ce^{141}, Ru^{103}, Zr^{95}-Nb^{95} and La^{140} were detected.

By 157 days only $Ce^{141,144}$, Ru^{103} and Zr^{95}-Nb^{95} were present in observable amounts.

The nuclides strongly adsorbed by the Chelex 100 column include $Ce^{141,143,144}$, Nd^{147} and La^{140}.* Of these La^{140}, with an easily identifiable peak at 1.60 Mev, was present in relatively high gamma abundance at times through 52 days after fission. Ce^{141} was present in relatively high gamma yield at early times and, along with Ce^{144} (both peaks at $\sim$ 0.14 Mev), increased with time to be the predominant peak at times longer than 150 days. Nd^{147}, strongly adsorbed by the resin (although

*Analyses of effluents taken during the course of the experiment indicated that these isotopes were essentially quantitatively retained by the resin during the seawater passage.

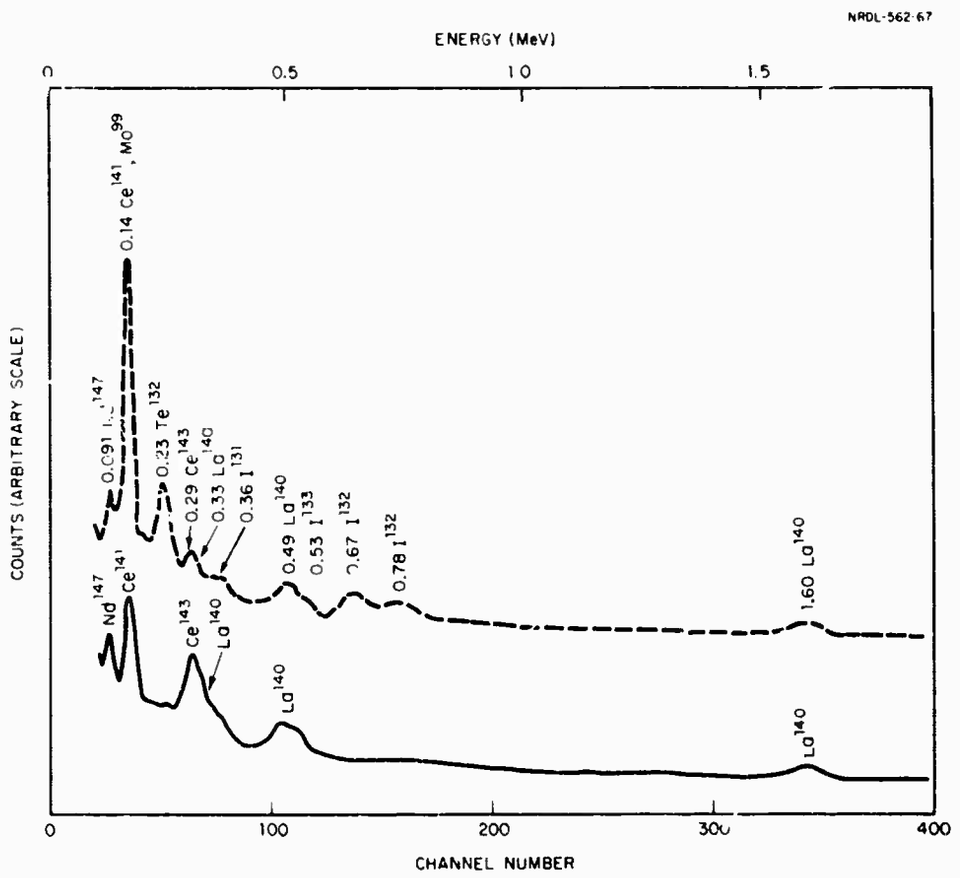

Fig. 1 Gamma Spectrum From Adsorbed Fission Products on Chelex 100 5 Days After Fission.

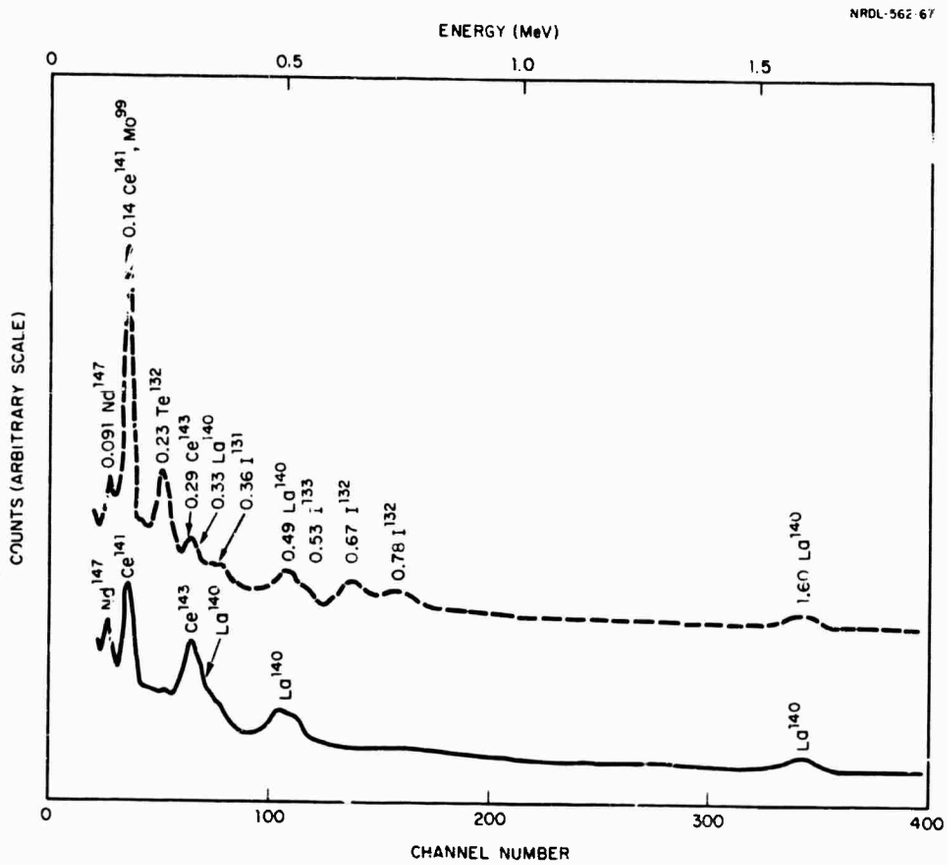

Fig. 1 Gamma Spectrum From Adsorbed Fission Products on Chelex 100 ½ Days After Fission.

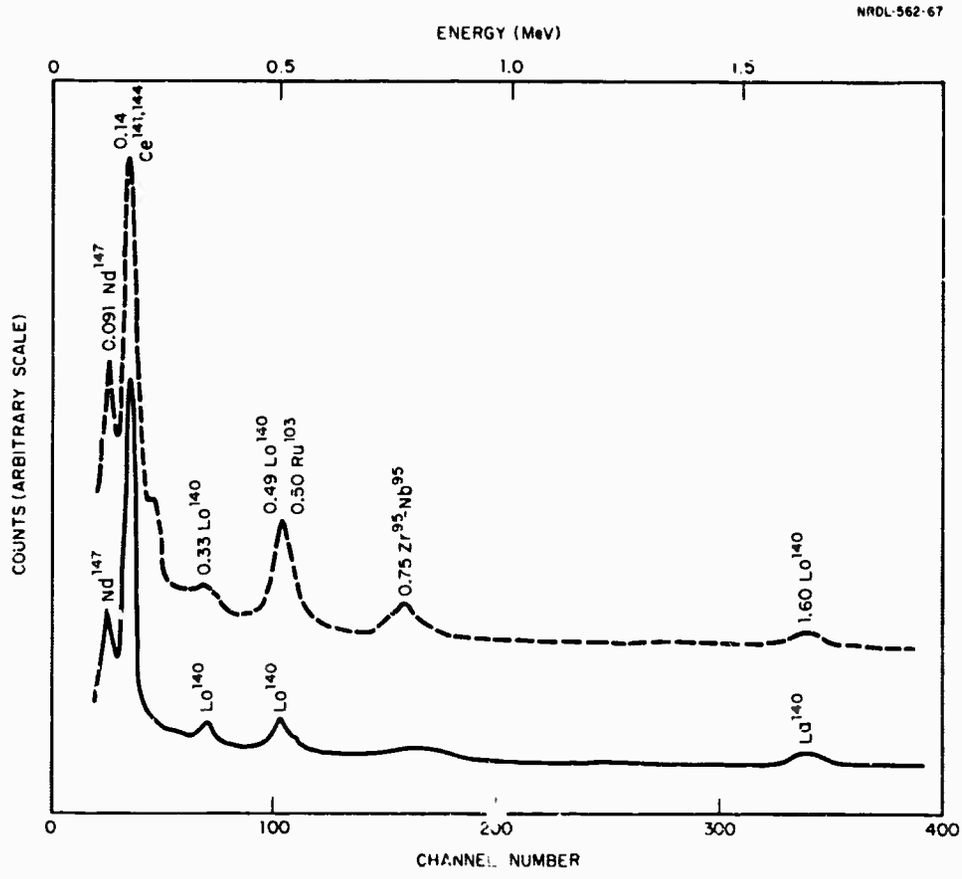

Fig. 3 Gamma Spectrum From Adsorbed Fission Products on Chelex 100 52 Days After Fission.

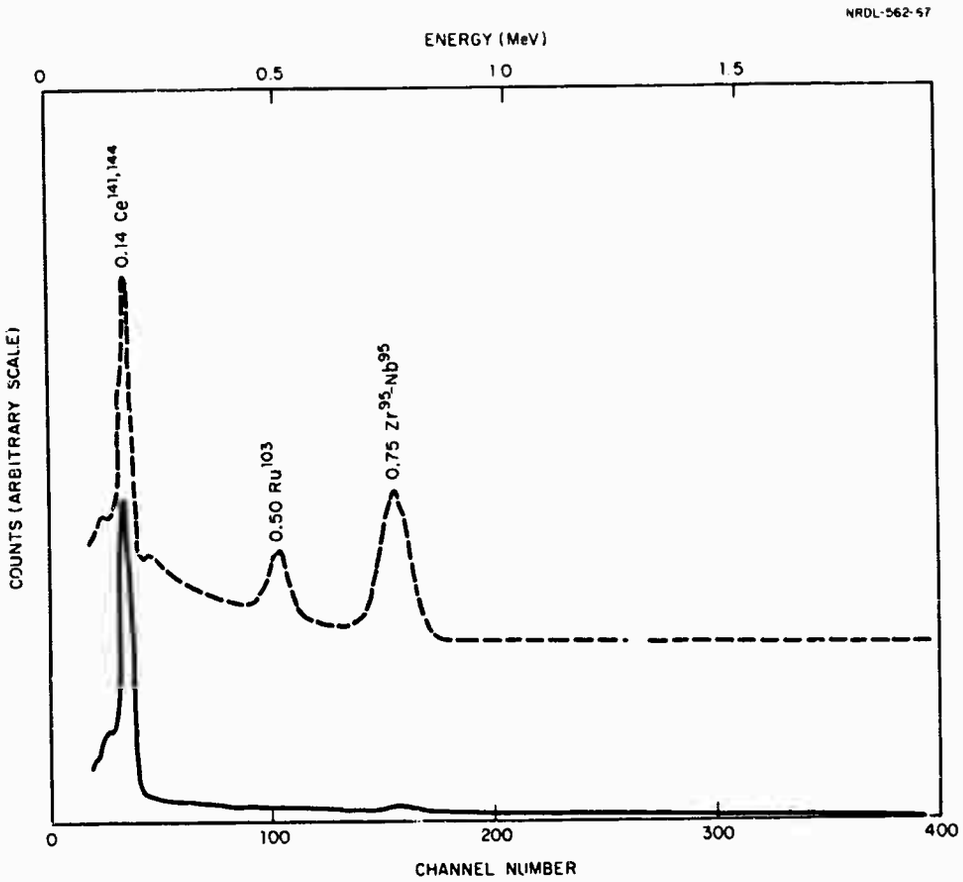

Fig. 4 Gamma Spectrum From Adsorbed Fission Products on Chelex 100 157 Days After Fission.

not in high gamma abundance), could be identified (0.091 Mev) through the 52 day sample. Ce^{143} was also observed at early times. However, its peak at 0.29 Mev was masked by the La^{140} peak at 0.33 Mev.

Several nuclides which contributed heavily to the gamma spectrum of the unprocessed fission product sample were not retained by the column. These included Mo^{99}*, Te^{132}, $I^{131,132,133}$, Ru^{103} and Zr^{95}-Nb^{95}. Iodine is an anion and was not expected to be adsorbed by the cation exchange resin. The others may either have been complexed by seawater component to some non-adsorbing state or exist in solution in colloidal form.

The results generally agree with those obtained in a previous report[14] except for the case of Ru^{103} and Zr^{95}-Nb^{95}. The adsorption on Chelex 100 for these radionuclides had been approximately 60 % in the previous study. This apparent contradiction can probably be related to the method in which the two experiments were conducted. The previous study utilized a limited bath technique in which 20 ml of seawater containing the radioactive tracer were equilibrated with 0.25 g of Chelex 100. In the present study 1 liter volumes of seawater containing the radioactive tracer were passed through a column. Since the adsorption coefficients[14] of Ru^{103} and Zr^{95}-Nb^{95} were only slightly higher than that of Ca, (concentration in seawater of approximately 0.4 g/liter), it was possible that when a sample containing a relatively large volume of seawater was passed through the column, the column became saturated with respect to Ca and this saturation of the column prevented the effective adsorption of the trace quantities of Ru, Zr and Nb. The radionuclides, which had much higher adsorption coefficients than Ca, were not noticeably affected. This hypothesis was further substantiated by the comparison of results obtained when 20 ml and 1 liter seawater samples containing 157 day-old fission products were passed through a column in separate experiments. Elution and analysis of the adsorbed activity showed that

*Based on results in Ref. 14.

approximately 50 % of the Ru^{103} and Zr^{95}-Nb^{95} was adsorbed from the 20 ml sample while no appreciable amounts of these radionuclides were adsorbed from the 1 liter sample.

2. Adsorption of Mixed Fission Products from Seawater at Designated Times After Fission.

Figure 5 shows that at 5 days after fission about 34 % of the total radionuclide gamma activity was retained by the column. The percent adsorption increased with time to reach a maximum of 50 % at 30-40 days after fission and then decreased to 40 % at 80 days and 36 % at 157 days after fission.

The reason for the increase at 30-40 days was the rapid percentage growth of the gamma contribution of the highly adsorbed La^{140} and Ce^{141} due to the decay of the shorter-lived isotopes. After 40 days La^{140} decayed at a faster rate than the percentage growth of $Ce^{141,144}$, thus giving a net decrease in the total radionuclide gamma activity adsorbed by the column.

3. Adsorption of Fission Products from Different Volumes of Seawater.

The results (Table 1) showed that the percent adsorption of gamma activity for fission product activity of age 52 days after fission was

TABLE 1

Column Efficiency as a Function of Sample Volume

Sample Volume (liters)	Radionuclide Gamma Activity Adsorbed (%)
1.0	47.8
5.0	47.4
20.0	47.1

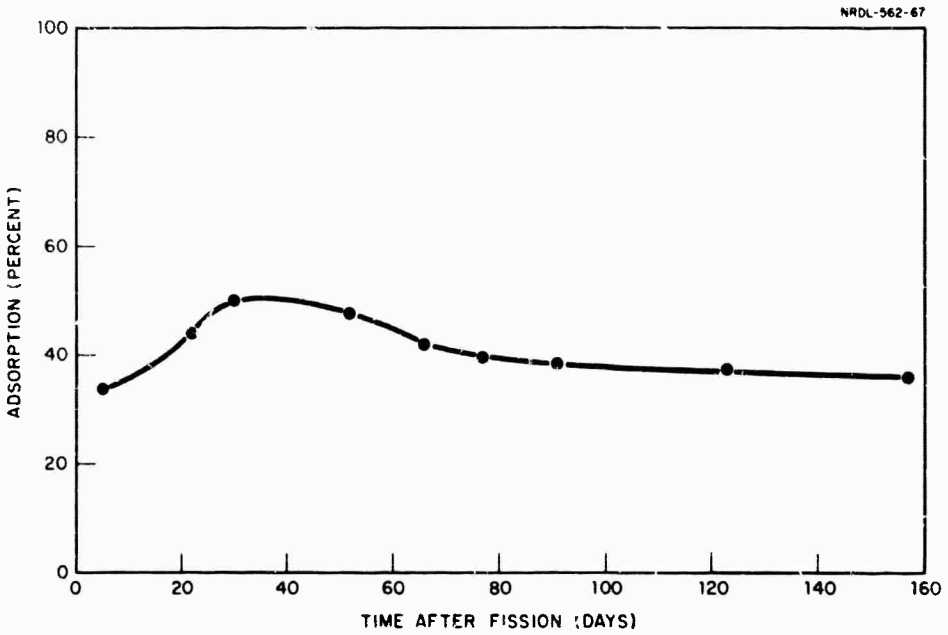

Fig. 5 Adsorption of Total Radionuclide Gamma Activity on Chelex 100.

essentially constant for volumes 1 to 20 liters. Elution and analysis of the adsorbed activity showed that it was primarily Nd^{147}, Ce^{141}, and La^{140}.

4. Effect of Flow Rate on the Efficiency of the Chelex 100 Column; La^{140} as Simulant for Fission-Product Activity.

The results are given in Fig. 6. At low flow rates, 12 ml/cm^2-min,* adsorption of La^{140} activity was almost quantitative for volumes up through 20 liters. At higher flow rates, the percent leakage** increased as larger volumes of solution were passed through the column. For flow rates of 26 and 60 ml/cm^2-min, a linear slope was obtained after passage of 2 liters of solution. In all cases the slope of the leakage curve was steeper for higher flow rates.

CONCLUSION

Results thus far obtained indicate that Chelex 100 can be used to concentrate trace quantities of fission product activities from seawater. Between 35 and 50 % of the total radionuclide gamma activity of the fission products are adsorbed by passage of seawater containing the mixed fission products through a column at a flow rate of 8 ml/cm^2-min. For higher flow rates column efficiency might be decreased. However, since larger volumes of water would be processed in a given period, the total amount of radionuclide gamma activity adsorbed by the column may be increased.

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* All other experiments (Parts 1, 2 and 3) done at 8 ml/cm^2-min.
**Percent of activity in 1 liter increment.

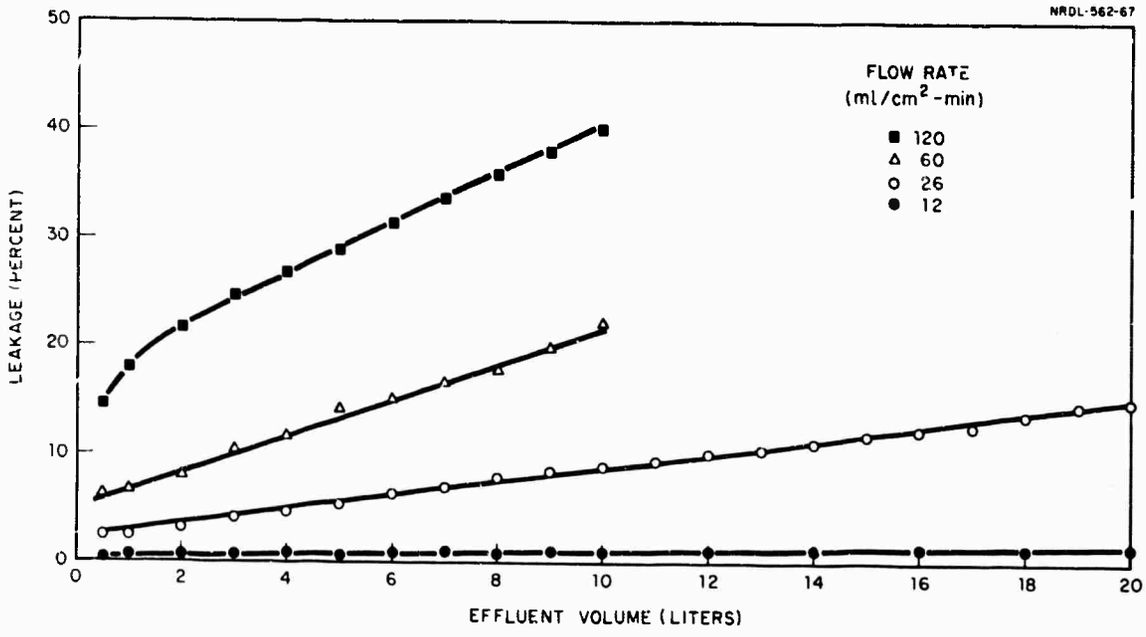

Fig. 6 Effect of Flow Rate on Column Leakage.

Optimizing the concentration system would necessarily involve trade-offs between column size, flow rate, sampling time and counting time. At any event, use of a concentration system in conjunction with a gamma counting or spectrometer system should considerably increase the detection sensitivity of an *in situ* monitoring system.*

This method, based on our laboratory study, appears to be suitable for the *in situ* operation in respect to efficiency, simplicity of operations, reliability, and speed. Nevertheless, further investigation, modification, and improvement should be made for the ultimate design of the actual system.

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UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)

U. S. Naval Radiological Defense Laboratory
San Francisco, California 94135

2a REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

3 REPORT TITLE

CONCENTRATION OF MIXED FISSION PRODUCTS FROM SEAWATER BY CHELEX 100

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

5 AUTHOR(S) (First name, middle initial, last name)

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Harry A. Goya

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
22 December 1967	32	14

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	USNRDL-TR-67-128
c. ARPA, Order No. 961, Amendment 1, Program Code 7F40.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Advanced Research Projects Agency Washington, D. C. 20301

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The effects of fission-product age, total seawater volume, and flow rate on adsorption were studied.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fission products						
Ion exchange						
Seawater						
Chelex 100						